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Research on Pretreatment Methods for Quantitative Detection of Polycyclic Aromatic Hydrocarbons in Soil

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Abstract

With the increasing practice of modern industrialization in society, the environmental pollution problems caused by persistent organic pollutants, especially polycyclic aromatic hydrocarbons (PAHs), have attracted widespread attention. PAHs are widely present in the incomplete combustion products of fossil fuels such as coal and oil, and may pose a threat to human health through the food chain. Therefore, accurate detection of PAHs in soil is extremely important for evaluating the environmental pollution status and its impact on human health. This study systematically investigated the pretreatment methods for PAHs in soil, compared the extraction efficiencies of the accelerated solvent extraction method (ASE) among different extraction techniques, and analyzed the impact of the concentration and purification techniques of the extract on the recovery rate. The study found that under specific temperature and pressure conditions, the optimized ASE technique can achieve a higher recovery rate of PAHs compared with the traditional Soxhlet extraction technique. This study provides effective technical support for environmental monitoring and risk assessment, and has important guiding significance for the scientific prevention and control of soil pollution and the improvement of environmental quality.

Keywords

Soil; Polycyclic Aromatic Hydrocarbons; Quantitative Detection; Pretreatment.

1. Introduction

Currently, the attention to polycyclic aromatic hydrocarbons (PAHs) in the field of environmental science is constantly increasing. These substances are mostly generated under the condition of incomplete combustion of organic substances such as coal and oil. Under specific conditions, PAHs can be photodegraded or biodegraded [1]. However, if the molecular weight of PAHs is relatively large, the levels of photolysis, hydrolysis or biodegradation are relatively low. Therefore, these compounds often migrate into the soil through dry and wet deposition and may threaten human health through the food chain. Thus, accurately detecting PAHs in soil has become an important topic in environmental monitoring.

2. Overview of Pretreatment Steps

In the complex soil matrix, the analysis of PAHs faces many challenges. The pretreatment process will directly affect the results. If it is not properly handled, the accuracy of the results will be reduced. Generally, the pretreatment process includes steps such as extracting samples, concentrating the extract, and purifying the extract [2].

Currently, there are quite a number of extraction techniques available. Some scholars have conducted a comparative analysis of the commonly used extraction techniques at present. The results show that the recovery rates and repeatability of Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction techniques are relatively similar; and there is no significant difference in the extraction rates of pressurized fluid extraction and ultrasonic extraction techniques. After comprehensive analysis, it is found that the ultrasonic extraction technique can accelerate the pretreatment speed by virtue of its simplicity and high efficiency, and also shows the advantage of low cost.

Before instrumental analysis, in order to reduce the interference of the matrix on the determination, reducing the extract to remove excess solvents and purification are crucial steps. Both rotary evaporation and nitrogen blowing techniques can achieve efficient concentration goals. In terms of purification, commonly used filling materials include silica gel, Florisil, etc. Although some studies have shown that omitting the purification step may not necessarily affect the recovery rate, if appropriate extraction methods and detection equipment are selected and the experimenters have sufficient experimental skills, effective PAHs analysis can also be achieved [3].

Among the PAHs detection techniques in soil, high-performance liquid chromatography (HPLC) and gas chromatography-mass spectrometry (GC-MS) are the two main instruments. HPLC can operate under the condition of low column temperature and is suitable for the quantitative analysis of PAHs, so it is favored. The combination of liquid chromatography and fluorescence detector is widely used due to its fast and accurate characteristics and can effectively detect the trace PAHs remaining in the soil.

The "Determination of Polycyclic Aromatic Hydrocarbons in Soil and Sediment - High-Performance Liquid Chromatography" (HJ 784—2016) stipulates the determination method of PAHs in soil and sediment. Researchers should choose suitable concentration and purification methods according to specific situations [4]. Although the purification step is not necessary for every analysis, research on concentration and purification methods is beneficial to improving the extraction efficiency of PAHs.

Based on this, this study selects ultrasonic extraction as the extraction method, dichloromethane as the extraction agent, and at the same time uses professional detection techniques to explore the impact on the recovery rates of 15 kinds of PAHs that are preferentially controlled by the US Environmental Protection Agency (USEPA), and also discusses the differences in the impacts caused by different concentration and purification methods, hoping to provide help for the analysis of polycyclic aromatic hydrocarbons.

3. Materials and Methods

3.1. Chemical Reagents and Materials Required for the Experiment

Ultra-pure water prepared by MilliQ was used; dichloromethane that reached analytical purity after redistillation (provided by Xilong Chemical Co., Ltd.); chromatographically pure acetonitrile sold by Thermo Fisher Scientific Inc.; anhydrous sodium sulfate obtained after baking at 400 °C for 4 h; HC-C18 column produced by Shanghai Anpel Laboratory Technologies Inc.

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3.2. PAHs Standard Solutions

Based on the standard sample numbered CDGG-110124-06 provided by Shanghai Anpel Laboratory Technologies Inc., a set of mixed standard solutions containing 16 kinds of PAHs was prepared. Specifically, they include naphthalene, acenaphthylene, acenaphthene,fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]pyrene and indeno[1,2,3-cd]pyrene. The initial concentrations of these 16 kinds of PAHs were all 200 mg/L. For the standard solutions, the researchers pipetted the corresponding volumes as needed and diluted them with acetonitrile into a series of standard mixed solutions with concentrations ranging from 16 to 320 μg/L. All the prepared solutions were stored in brown bottles and placed in a light-proof environment at 4 °C to ensure their stability.

3.3. Spike Recovery Rates of Different Methods

For the 0 - 20 cm soil layer of a certain vegetable garden, the author carried out the collection of soil samples. The collected samples were preliminarily screened and decontaminated, and then freeze-dried and stored in a desiccator for subsequent analysis. The experimental process was as follows.

Accurately take out 1.0 g from the sample as the test sample, and then place it in a 40 mL brown glass container with a polytetrafluoroethylene liner and a lid. Add 1 mL of the PAHs standard solution with a concentration of 800 μg/L to the sample, and use the dichloromethane solution without PAHs as a control. Place the opened sample bottle in a fume hood and let it stand until the dichloromethane in it has fully evaporated. To remove water, add 1.0 g of anhydrous sodium sulfate. After adding 10 mL of dichloromethane, the test sample was placed in a numerically controlled ultrasonic cleaner for ultrasonic extraction for 2 h.

After the extraction was completed, the supernatant was separated by centrifugation, and then three different methods were used for differential treatment, and each concentration and purification method was repeated three times.

In the first method, dichloromethane extract and acetonitrile were added to the chromatographic vial (with a specification of 2 mL) in a ratio of 2:1 in turn. After uniform stirring, nitrogen blowing was carried out to reduce the risk of PAHs loss due to solvent evaporation. When the concentrated solution was reduced to about 0.25 mL, 1 mL of acetonitrile was added again and nitrogen blowing was repeated until the solvent was completely converted into acetonitrile. After completing the above steps, the sample was filtered through a 0.22 μm organic microporous filter membrane and placed in a chromatographic vial for subsequent analysis.

The other two methods involved the process of distilling dichloromethane into acetonitrile. Add 5 mL of the dichloromethane extract to a 100 mL round-bottomed flask and gradually evaporate it to about 1 mL using a rotary evaporator. Then, add 1 mL of acetonitrile three times until the dichloromethane was completely replaced by acetonitrile. One of the methods directly filtered the concentrated sample and then saved it; the other method adopted the solid-phase extraction technique and used a self-made C18 solid-phase extraction column to filter the standard solution with a concentration of 800 μg/L.

3.4. Chromatographic Analysis Conditions

In this study, high-performance liquid chromatography (UPLC) was used to conduct an in-depth exploration of PAHs. The chromatographic column was ACQUITY UPLC BEH Shield RP18 (150 mm × 2.1 mm × 1.7 μm). This technology is widely used in the rapid detection of complex organic substances due to its characteristics of high resolution and rapid analysis. The column temperature of 45 °C ensured that the analytes could interact better with the stationary liquid

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phase under optimized conditions and improved the separation efficiency. The injection volume was set at 3 μL, which was a careful consideration for the accuracy and repeatability of the analysis.

Acetonitrile and ultrapure water were chosen as the mobile phase mainly based on their strong dissolving ability and chromatographic dilution ability, which were particularly crucial for obtaining excellent component separation and reproducibility. The gradient elution program was as follows: from 0 to 6.8 min, 50% acetonitrile; from 6.8 to 8.3 min, the acetonitrile increased from 50% to 67%; from 8.3 to 10.8 min, 67% acetonitrile; from 10.8 to 14.0 min, the acetonitrile increased from 67% to 77%; from 14.0 to 18.5 min, the acetonitrile decreased from 77% to 50%. The wavelength change program of the fluorescence detector referred to the research of Ni Jinzhi et al. [5]. The running flow rate of the mobile phase was set at 0.4 mL/min.

The introduction of the gradient elution technique could effectively prevent the overlap of analytes, and the wavelength change of the fluorescence detector provided more possibilities for improving the detection sensitivity and enriching the selectivity. The external standard method was used for quantitative analysis, which played a key role in confirming and evaluating the content of PAHs in environmental samples and further provided reliable data for environmental monitoring and risk assessment.

The UPLC-FLR method described in this study effectively improved the analysis efficiency of PAHs by virtue of its characteristics of being fast, efficient and accurate, and contributed important technical support and a data basis to the research in related fields. The application of this method not only promoted the development of the fields of environment and ecological chemistry but also deepened the understanding of the migration and transformation mechanisms of pollutants in the environment, providing a scientific basis and practical tools for protecting the environment and controlling and reducing PAHs pollution. In the continuous efforts to protect the environment, the technical means provided by this study is particularly important.

4. Results and Discussion

4.1. Selection of Extraction Methods and Extractants

In the current research, ultrasonic technology is regarded as an effective method for extracting PAHs from soil and sediments. Scholars have conducted multiple comparative experiments aiming to explore the impact of different extraction methods and extractants on the extraction efficiency of PAHs.

Some scholars compared three different methods, namely Soxhlet extraction, ultrasonic extraction and solid-phase extraction, in their research and found that the Soxhlet extraction method using a mixed solvent of acetone and n-hexane (with a volume ratio of 1:1) had the highest extraction efficiency. In addition, the ultrasonic-assisted extraction technique also showed good performance, with a recovery rate ranging from 89% to 93%. Further analysis indicated that in some cases, the efficiency of ultrasonic extraction was higher than that of Soxhlet extraction. For example, for most of the 16 kinds of PAHs, except that the recovery rate of naphthalene was slightly lower in ultrasonic extraction, the rest were all between 90% and 110%, while the optimized supercritical fluid extraction method (SFE) was only about 80%, and the recovery rate of benzo[a]pyrene was obviously lower.

In terms of the selection of extractants, solutions such as dichloromethane, acetone, and n-hexane will all have an impact on the recovery rates of PAHs. Some scholars took the Soxhlet extraction method as the extraction method and the polycyclic aromatic hydrocarbons in soot and sediments as the research objects, and respectively studied the impact of seven organic solvents on the extraction efficiency of PAHs. Among them, compared with other solvents, the mixed solvent of toluene and methanol (with a volume ratio of 1:1) had the largest difference

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in the recovery rates of 13 kinds of PAHs, which could reach 16%. When exploring the impact of multiple solvents on the extraction effect of PAHs in atmospheric particulate matter, it was found through research and comparison that the mixed solvent of n-hexane and dichloromethane prepared in a ratio of 1:1 had the most prominent extraction effect.

4.2. Impact of Different Concentration and Purification Methods on the Recovery Rates of PAHs

This study focused on the core issue of using multiple pretreatment techniques for the extraction of PAHs in soil samples and the comparison of recovery rates. By adding standard compounds to soil samples containing PAHs, the concentration of the target compounds was brought to the level of 800 μg/kg. During the extraction process, dichloromethane was used as the solvent, and dissolution was completed with the help of ultrasonic equipment. For the extracted sample solutions, this study adopted three different concentration and purification techniques for treatment and conducted a comprehensive analysis of the results.

The research results showed that among the PAHs detected, naphthalene, as a typical low-ring compound, had a relatively low recovery rate, ranging from 65.9% to 71.9%. For the other PAHs substances, in the first method, through nitrogen blowing for concentration and filter membrane for impurity removal, the recovery rate ranged from 75.4% to 102.9%; in the second method, through rotary evaporation for concentration and filter membrane for impurity removal, the recovery rate ranged from 85.9% to 111.1%; in the third method, through rotary evaporation for concentration and additional purification by the C18 solid-phase extraction column, the recovery rate ranged from 80.8% to 104.4%.

Through comparison, it was found that although all of the above three methods could meet the requirements for the quantitative analysis of PAHs in soil, in terms of the recovery rates of 2- and 3-ring PAHs, the nitrogen blowing method performed relatively weakly. Relatively speaking, the rotary evaporation method was more capable of strengthening the recovery effect of these low-volatile PAHs. Here, it was necessary to focus on the accurate adjustment of the water bath temperature and the corresponding changes in the negative pressure.

Compared with the second method, the third method could effectively separate the target compounds from impurities and improve the recovery rate of PAHs components by using the C18 solid-phase extraction column for purification. It thus indicated that the recovery rate of samples purified by the C18 solid-phase extraction column was the most ideal, and this study provided a practical reference for the selection of appropriate pretreatment techniques.

4.3. Quantitative Analysis of PAHs in Field Polluted Soil

This study aimed at the soil pollution status around steel plants and achieved the quantitative analysis of PAHs by using three different concentration and purification techniques. The analysis results clearly showed that when using the methods studied in this paper, the measured values and spike recovery rates of samples treated by nitrogen blowing for concentration, rotary evaporation for concentration combined with purification by the C18 solid-phase extraction column remained consistent. However, during the nitrogen blowing treatment, affected by the evaporation of the solvent, the content of PAHs might be reduced, resulting in relatively low results in the quantitative analysis. On the contrary, if the absorption was incomplete during the purification process by the C18 solid-phase extraction column, the obtained results might be on the high side. After comprehensive consideration, after ultrasonic extraction of PAHs in soil, the combined application of rotary evaporation technology and purification by the C18 solid-phase extraction column could be recommended as a measure suitable for the treatment of such soil samples.

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5. Conclusion

PAHs are common organic pollutants in the research on soil environmental pollution, and their extraction methods and efficiencies directly affect the accuracy of data analysis. When analyzing these compounds, the choice of pretreatment techniques plays a key role in the extraction efficiency of PAHs. However, it was found in practice that the nitrogen blowing method was prone to cause the loss of target compounds during the process of concentrating the PAHs extract. On the contrary, the rotary evaporation method could operate at a relatively low temperature and appropriate pressure, significantly reducing the volatilization and loss of PAHs components. Meanwhile, its operation process was simple and easy to master. In addition, using the C18 solid-phase extraction column to purify the extracts was helpful for enhancing the separation effect of compounds and improving the precision of quantitative analysis. Through comprehensive evaluation of the performance of various pretreatment methods in terms of recovery rates and the quantitative analysis of PAHs in field polluted soil, the scheme combining rotary evaporation for concentration and treatment by the C18 solid-phase extraction column had outstanding performance in terms of operation convenience, efficiency, and result reliability.

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